Recrystallization and investigation of bismuth thin films by means of electron beam in transmission electron microscope

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Recrystallization and investigation of bismuth thin films by means of electron beam in transmission electron microscope

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Abstract. Thin bismuth films obtained by vacuum deposition were recrystallized under electron beam of scanning electron microscope at 5 kV and examined in a transmission electron microscope at 200 kV. In recrystallized films, various microstructures were detected: single-crystal, polycrystalline and amorphous regions, more or less faceted grains, single crystals and untransparent drop-shaped particles. In the crystallized film, a strong internal bending of the crystal lattice is detected, up to 110 deg/μm.

1. Introduction

The properties of thin films differ significantly from the properties of bulk material. A small thickness causes some classical and quantum size effects [1]. Due to the effect of magnetoresistance, thin bismuth films are used in magnetic field measuring devices. In addition, single-crystal thin films of bismuth have thermoelectric properties, and also find application in radiation detectors. Thin films of bismuth and its compounds are now actively being investigated and in connection with their unusual quantum properties [2, 3].

The properties of thin bismuth films strongly depend on the grain size of the film. The size of the crystallites, in turn, depends on the conditions for obtaining the film: the method of deposition, the type of substrate. Single-crystal films required for some applications can usually be obtained by deposition on a single-crystal high-purity substrate under balance conditions [2, 3].

Single-crystal films of bismuth and its compounds can be obtained from initially polycrystalline films by annealing [4]. An electron beam of the electron microscope can be useful for local annealing (see, e.g. [5-8]).

In an electron microscope, the beam intensity sufficient to recrystallize or change the phase state of thin films of many materials: oxides, chalcogenides, semiconductors, low-melting metals can be achieved. The results of the beam action can be imaged directly after or even during the experiment. The purpose of this work was to test the possibility of recrystallization of thin bismuth films using electron beam inside a microscope column and to study their microstructure before and after annealing in transmission electron microscope (TEM).

2. Experiment

2.1. Samples preparation

A sample for the study was obtained by thermal evaporation of chemically pure bismuth in a vacuum on a mica substrate coated with amorphous carbon sublayer to avoid influence of single crystalline

mica on the formation of bismuth film. Then the resulting Bi films was separated from the substrate on the distilled water surface and placed on standard copper grids for TEM.

2.2. Electron beam exposure

The exposure of the film was initially carried out by an electron beam in a JEM-2100 microscope in TEM mode at an accelerating voltage of 200 kV using different diaphragms and condenser currents and different beam sizes, but the film remained stable, no visible changes were observed. The experiments were then carried out in a scanning electron microscope (SEM) LVEM-5 with field emission gun (FEG) at an accelerating voltage of 5 kV in reflected mode in a number of areas of the object TEM grid. The irradiation time was from a few seconds to 10 seconds and more. The result was the melting of the film with partial evaporation and further recrystallization of bismuth. At an exposure time of 4 s or less, traces of melting and recrystallization were not detected. When exposed for 5 s, the zones of recrystallization and melting with partial evaporation of several μm^2 are distinguishable, figure 1a–b. When exposed for 10 seconds or more, a carbon supporting sublayer become visible over the beam scanning area, figure 1c–d.

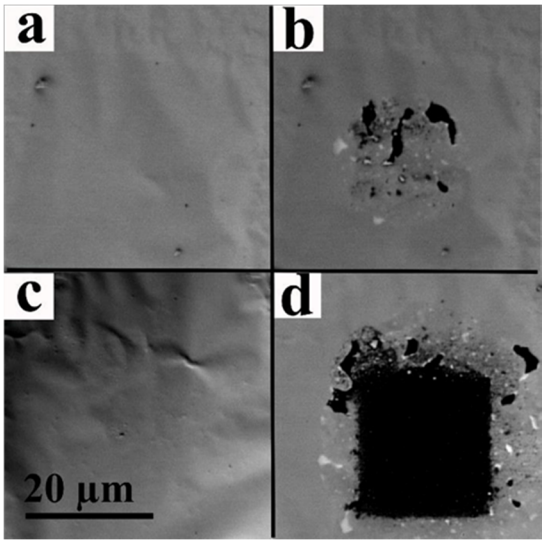

Figure 1. LVEM-5 SEM images in backscattered electrons: film area before e-beam exposure (a); film area after the exposure for 5 s (b); other film area before e-beam exposure (c); the same area after the exposure for 10 s (d).

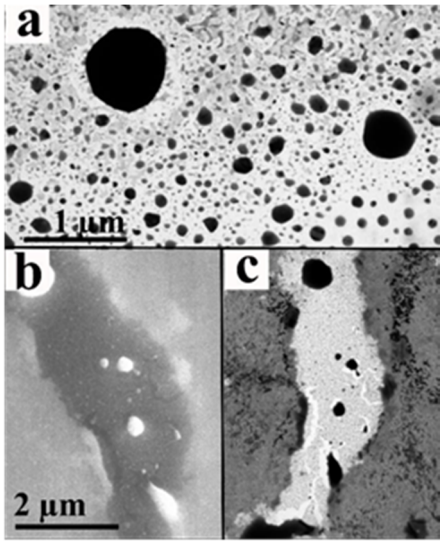

Figure 2. JEM-2100 images: drop-shaped particles of bismuth in the region of partial evaporation of the film (a); region of partial evaporation in the scanning mode (backscattered electrons) (b); region in the transmission mode TEM (c).

2.3. TEM of bismuth films

According to TEM, the initial film is polycrystalline, with crystallite sizes ranging from ~10 to 200 nm.

After irradiation, the film was also examined in a TEM JEM-2100 with an accelerating voltage of 200 kV. The investigation was carried out in the modes of bright and dark fields, selected area diffraction, and SEM mode (with scanning module for detecting secondary and backscattered electrons).

TEM images show that in the partially evaporated film regions, bismuth is condensed into large droplets of round shape, ranging in diameter from about 50 nm to 1 μm. Droplets having a diameter of

about 100 nm or more are partially or completely not transparent to the electron microscope beam, figure 2a–c. It is well known in TEM that it corresponds to thicknesses around 0.1 μm and above.

Also, based on the results of comparison of the images in a bright field and a dark field with using the sector of amorphous halo of an electron diffraction pattern, an amorphous net formed on a substrate after electron beam irradiation is revealed, figure. 3a–b. The width of the lines of this net is of the order of 10-20 nm, the size of the cells corresponds to the dimensions of the crystals in the original polycrystalline film.

A small part of the material has crystallized in the form of separate faceted crystals lying on a carbon film, figure 4. These crystals have size up to several dozens of nm and mainly rhombic or hexagonal motifs of faceting.

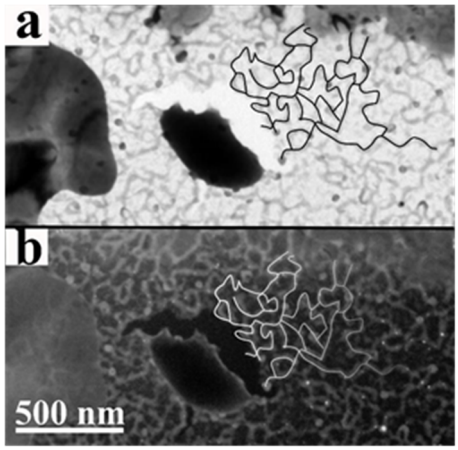

Figure 3. TEM images with amorphous net in the region of partial evaporation (the net is visualized by white line contours drawn at the center): in the bright field mode (a); in the dark field mode (using the sector of amorphous halo) (b).

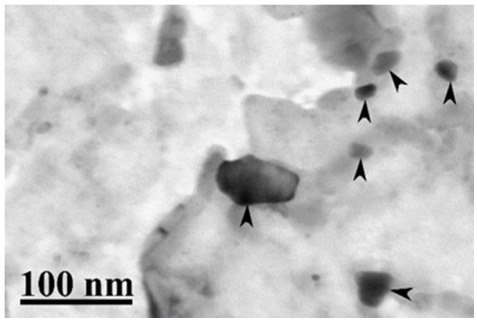

Figure 4. Faceted bismuth crystals (highlighted by arrows) formed on the substrate in the region of partial evaporation.

At the boundaries of the annealing zone, large bismuth single crystals with rounded edges formed up to several microns, figure 5a–b. The thickness of these single crystals from the measurements in a dark field is estimated to be within 30 nm (see details and equation (2) below).

In most of the crystallites of both the initial and annealed films, extinction bend contours are observed, figures 5 and 6, indicating a significant internal bending of the crystal [8]. Corresponding measurements were made of the internal bending of the crystal lattice in regions along bend contours. For each contour, measurements were taken at 1-3 points. The calculations were carried out according to the following formula [8] (using $D = (d_{hkl})^{-1}$):

$$R = 2N\,(\lambda D)^{-1} \tag{1}$$

where R is the bending radius of the lattice, N is the distance between the bend contours in the pair in the bright field $(\pm\ h\ k\ l)$, d_{hkl} is interplanar distance, D is the distance between the symmetrical reflexes of the electron diffraction pattern, λ-wavelength of the electron (0.0025 nm for 200 kV). The results are shown in table 1.

Estimates of the film thickness gave 10-20 nm according to procedure based on measuring bend contours fine structure [9]

$$t = 4N\,(\lambda n D^2)^{-1} \tag{2}$$

where t is the thickness of the film, n is the distance between the secondary maximums of corresponding bend contour in the dark field.

In the film before annealing, the value of the corresponding lattice misorientation gradient lies in the range from 7 to 110 deg/μm. Crystallites with bend contours are also located in the regions on the boundaries of the film, where potential mechanical bending could relax, figure 6, which additionally indicates internal bending, often observed during the crystallization of thin initially amorphous films. Single crystals after recrystallization have an internal lattice bending of 10 deg/μm and more, also obviously not associated with mechanical deformation. In large monocrystalline fields, a bending of ~ 60 deg/μm is observed.

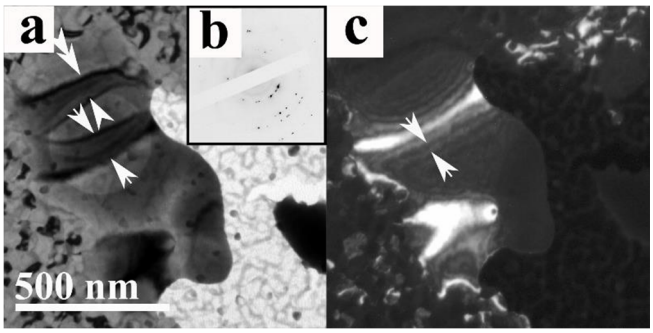

Figure 5. A single crystal with extinction bend contours on the boundary of the melting zone: TEM image in the bright field mode, pairs of bend contours (± *h k l*) are indicated by arrows (a); electron diffraction pattern of the selected region (b); TEM image in the dark field mode, arrows indicate secondary maximums of the intensity of the bend contour (c).

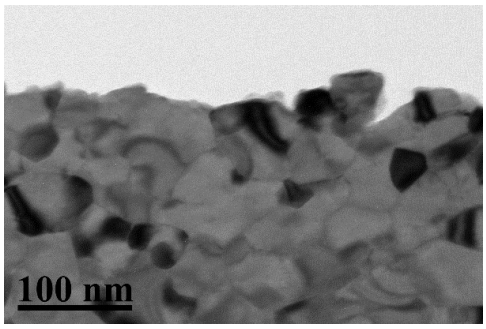

Figure 6. Crystallites with bend extinction contours near the disruption of the film.

Table 1. Results of measurements of the internal bend of the crystal lattice on some bend contours.

Measuring point No	*N* (nm)	*D* (nm^{-1})	*R* (μm)	Local internal bend (deg/μm)
1	15	10.9	1.1	53
	12	10.9	0.9	63
2	38	15.4	2.0	29
	29	15.4	1.5	38
3	12	15.2	0.7	88
	21	15.2	1.1	51
4	13	15.1	0.7	83
	18	15.1	1.0	59
5	20	15.0	1.1	55
	19	15.0	1.0	57
6	18	15.8	0.9	62
	10	8.9	0.9	67
	6	8.9	0.5	110
7	181	15.3	9.5	6
	146	15.3	7.6	8
	88	15.3	4.6	12

The formation of large single crystals is also observed, figure 7a–b. On the side opposite the melting and recrystallization zone, single crystals are adjacent to the original polycrystalline film, figure 5a. In the regions near the edges of the melting zones, close to large single crystals, in some single crystalline areas up to several μm in size were formed, figure 8. Visually on the TEM images they are often more transparent than surrounding thin film, that means they are much thinner thicker.

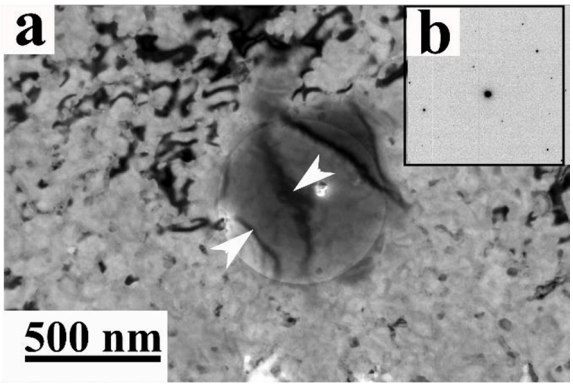

Figure 7. A large single crystal: TEM image in the bright field mode, arrows indicate pair (± *h k l*) of bend contours (a); corresponding selected area electron diffraction pattern (b).

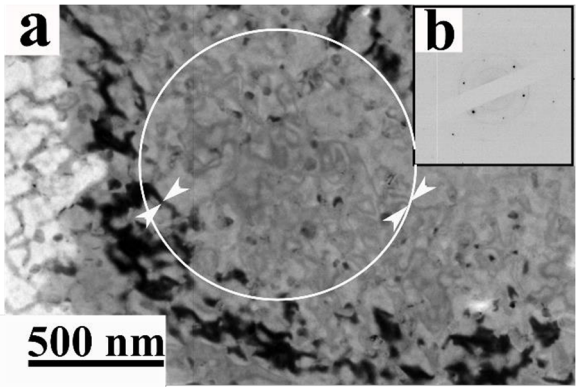

Figure 8. A single crystalline area near the zone of partial film evaporation: TEM image in the bright field mode, arrows indicate some pairs (± *h k l*) of bend contours (a); corresponding selected area electron diffraction pattern (b).

3. Results and Conclusion

Polycrystalline bismuth films with crystallite sizes ranging from 10 to 200 nm are subject to recrystallization under a beam of an electron microscope with FEG at low accelerating voltage. In this case, heterogeneous different single-crystal and amorphous structures are formed: more or less faceted single crystals (size 10-100 nm), single-crystalline areas (1-10 μm), round-shaped particles (50 nm – 1 μm) exceeding essentially the initial film thickness and net of amorphous material in strongly irradiated regions.

In thin crystallized bismuth films, internal bending of the crystal lattice is observed, varying from low values, ~10 deg/μm, to strong magnitudes, exceeding 100 deg/μm. Previously, it was discovered [8] as characteristics of specific crystallization from initial amorphous state in thin films and probably it can be the case for Bi films studied.

Acknowledgments

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